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NOTE ON KIRCHHOFF'S LAW.

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NOTE ON KIRCHHOFF'S LAW.

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Kirchhoff's Law in its simple statement says that the energy radiated at a given temperature divided by the absorption coefficient for that temperature is the same for all bodies of the same shape and size, that is, equal to the energy radiated by a perfectly absorbing body of the same shape and size at that temperature. The relation is easily shown to hold for total radiation, and depends merely on the First and Second Laws of Thermodynamics. But for separate wave lengths, a reduction of the law to a firm thermodynamic basis, though often attempted,[1] seems not to have been completely obtained. Unwarrantable assumptions, sometimes tacit, seem unavoidably to have been introduced.

The present paper, in order to show the nature of the assumptions that must be introduced, attempts to set up a system of assumptions from which the law will rigidly follow.

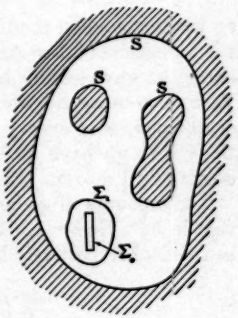

Figure 1.

Pursuing in the main a method of proof due to E. Pringsheim,[2] we take now a body S, in which there is a cavity (see Figure 1). This body need not be all in one piece nor need the cavity be filled homogeneously with one medium. Suppose, however, that there is in the cavity a simple closed surface Σ_1, enclosing another closed surface Σ_0 and not touching it at any point. The space between Σ_0 and Σ_1 is supposed filled with a medium

[1] For such considerations see H. Kayser: Handb. der Spectroscopie, II, 13 ff.

[2] E. Pringsheim: Einfache Herleitung des Kirchhoffschen Gesetzes, Verh. deutsche Phys. Ges. **3**, 81. Also Kayser: Spectroscopie, p. 37.

For a criticism of this proof see M. P. Rudski: Zeitschr. f. Wiss. Photog. **3**, 217, 1905. A reply by Pringsheim, ibid. p. 281.

that is fixed rigidly with Σ_1 wherever in the cavity Σ_1 may be. Σ_0 is fixed rigidly in this medium. We shall regard Σ_0 as a slab whose dimensions are small in regard to the other dimensions of the cavity, and whose thickness is small in comparison to its width and height. This surface Σ_0 we consider filled with various substances; we may have it so that the two faces consist of different materials. Let us denote the two surfaces by σ_1 and σ_2, each of area σ.

We have two quantities of energy to consider in regard to Σ_0, that which passes out of Σ_0, and that that passes in. The amounts of energy that in unit time pass out of Σ_0 at wave lengths between $\lambda = a$ and $\lambda = b$ through the two faces σ_1 and σ_2 we can denote respectively by

$$\sigma \int_a^b E_{\sigma_1}(\lambda)\, d\lambda + H_{21} \Big]_a^b \tag{1}$$

and

$$\sigma \int_a^b E_{\sigma_2}(\lambda)\, d\lambda + H_{12} \Big]_a^b \tag{2}$$

where $E_{\sigma_1}(\lambda)$ and $E_{\sigma_2}(\lambda)$ are functions of the substance of the element of surface, of its temperature, and of the nature of the medium in which it is immersed, but not of the temperature or position of other bodies in its neighborhood. $H_{21}\Big]_a^b$ and $H_{12}\Big]_a^b$ are two functions that depend on the surrounding conditions and approach zero as Σ_0 is removed from the influence of other radiating bodies; they represent the amounts of energy at wave lengths between $\lambda = a$ and $\lambda = b$, transmitted through Σ_0 from σ_2 to σ_1 and from σ_1 to σ_2 respectively. We shall denote the total amounts of energy transmitted by H_{21} and H_{12}. These assumptions that we have made in regard to $E_{\sigma_1}(\lambda)$ and $E_{\sigma_2}(\lambda)$ constitute essentially Prevost's Law of Exchange.

The amounts of energy at wave lengths between $\lambda = a$ and $\lambda = b$ that in unit time reach Σ_0 at the two faces σ_1 and σ_2 from outside, we can denote respectively by

$$\sigma \int_a^b e_{\sigma_1}(\lambda)\, d\lambda \tag{3}$$

and

$$\sigma \int_a^b e_{\sigma_2}(\lambda)\, d\lambda, \tag{4}$$

and the total amounts of energy that in unit time enter Σ_0 through the two faces σ_1 and σ_2 respectively by

$$\sigma \int_b^\infty A_1(\lambda)\, e_{\sigma_1}(\lambda)\, d\lambda + H_{12} \tag{5}$$

and

$$\sigma \int_b^\infty A_2(\lambda)\, e_{\sigma_2}(\lambda)\, d\lambda + H_{21}. \tag{6}$$

$A_1(\lambda)$ and $A_2(\lambda)$ are called absorption coefficients and denote functions that depend on the nature and temperature of σ_1 and σ_2, and possibly on the temperature of the body S. The existence of such functions is assumed. In the physical case the functions E, e, and A seem to be continuous in λ. And accordingly although it is not strictly necessary for the development of the proof, we shall make this assumption. We assume also that the functions E, e, and A are positive or zero at every λ, and that the functions A are $\leqq 1$.

Before seeking to obtain relations among the several kinds of energies, it is well to consider more in detail the nature of the functions $e_{\sigma_1}(\lambda)$ and $e_{\sigma_2}(\lambda)$. Let us denote by $\sigma \int_0^\infty e_1(\lambda)\, d\lambda$ the amount of energy that would reach σ' — the section of Σ_0 half way between σ_1 and σ_2 — from the σ_1 side, and $\sigma \int_0^\infty e_2(\lambda)\, d\lambda$ the amount of energy that would reach σ' from the σ_2 side, if Σ_0 were filled merely with the same medium that occupies the space between Σ_0 and Σ_1.

Let

$$e_{\sigma_1}(\lambda) = e_1(\lambda) + \delta_{\sigma_1}(\lambda) \tag{7}$$

$$e_{\sigma_2}(\lambda) = e_2(\lambda) + \delta_{\sigma_2}(\lambda). \tag{8}$$

Now as we change the slab Σ_0 in size, the functions $\delta_{\sigma_1}(\lambda)$ and $\delta_{\sigma_2}(\lambda)$ will change. If the body Σ_0 is small, the energy that reaches it will depend little on its own influence,[3] and $\delta_{\sigma_1}(\lambda)$ and $\delta_{\sigma_2}(\lambda)$ will be small. We make the assumption that as Σ_0 approaches zero, keeping the same relative proportions, both σ_1 and σ_2 approach zero, and approach zero in such a way that

$$\Delta_{\sigma_1} = \int_0^\infty |\, \delta_{\sigma_1}(\lambda)\, |\, d\lambda$$

and (9)

$$\Delta_{\sigma_2} = \int_0^\infty |\, \delta_{\sigma_2}(\lambda)\, |\, d\lambda$$

both approach zero.

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[3] See, however, p. 103.

Let us now put our apparatus in operation. At the start we put everything that has a temperature (ether, of course, has not) at one temperature T, and throughout succeeding time maintain S at temperature T. The body Σ_0 will thereafter, according to the Second Law of Thermodynamics, remain at temperature T. According to the First Law of Thermodynamics the amounts of energy absorbed and emitted by Σ_0 are equal. We have then the equation

$$\sigma\int_0^\infty E_{\sigma_1}(\lambda)\,d\lambda + H_{21} + \sigma\int_0^\infty E_{\sigma_2}(\lambda)\,d\lambda + H_{12} = \tag{10}$$
$$\sigma\int_0^\infty A_1(\lambda)\,e_{\sigma_1}(\lambda)\,d\lambda + H_{12} + \sigma\int_0^\infty A_2(\lambda)\,e_{\sigma_2}(\lambda)\,d\lambda + H_{21}$$

or

$$\int_0^\infty E_{\sigma_1}(\lambda)\,d\lambda + \int_0^\infty E_{\sigma_2}(\lambda)\,d\lambda = \int_0^\infty A_1(\lambda)\,e_{\sigma_1}(\lambda)\,d\lambda + \int_0^\infty A_2(\lambda)\,e_{\sigma_2}(\lambda)\,d\lambda. \tag{11}$$

We can at this point deduce that

$$\int_0^\infty E_{\sigma_1}(\lambda)\,d\lambda + \int_0^\infty E_{\sigma_2}(\lambda)\,d\lambda = \int_0^\infty A_1(\lambda)\,e_1(\lambda)\,d\lambda + \int_0^\infty A_2(\lambda)\,e_2(\lambda)\,d\lambda. \tag{12}$$

For if this equation did not hold, but if, on the other hand, the left hand member were equal to the right hand member plus a quantity ϵ, we could by taking Σ_0 small enough secure a contradiction from equation (11), and the assumption that Δ_{σ_1} and Δ_{σ_2} approach 0 as Σ_0 decreases indefinitely.

If we replace S by any other solid body fulfilling the conditions we get an equation

$$\int^\infty E_{\sigma_1}(\lambda)\,d\lambda + \int_0^\infty E_{\sigma_2}(\lambda)\,d\lambda = \int_0^\infty A_1(\lambda)\,e_1'(\lambda)\,d\lambda + \int_0^\infty A_2(\lambda)\,e_2'(\lambda)\,d\lambda. \tag{13}$$

The question now arises as to what is the relation among the e's, — $e_1(\lambda)$, $e_2(\lambda)$, $e_1'(\lambda)$, $e_2'(\lambda)$. If the functions $A_1(\lambda)$ and $A_2(\lambda)$ were perfectly arbitrary it could easily be shown that all the functions $e(\lambda)$ are identical; but we have no right to make such an assumption.[4]

[4] See page 104. This is in fact the assumption in the proof of E. Pringsheim.

The principal difficulty of the proof lies precisely in this step. The purpose is to make as modest a requirement as possible for the function $A(\lambda)$. We shall assume that there exist, or can be constructed, physical bodies such that the resulting assemblage of absorption coefficients is what we may call densely distributed between some two absorption coefficients that are distinct for every value of λ. We define densely distributed as follows:

Let $A'(\lambda)$ and $A''(\lambda)$ be two functions positive or zero and continuous for all positive values of λ. Let $f(\lambda)$ be any function finite and continuous for all positive values of λ, such that

$$A'(\lambda) \geqq f(\lambda) \geqq A''(\lambda), \qquad \lambda > 0,$$

or

$$A'(\lambda) \leqq f(\lambda) \leqq A''(\lambda), \qquad \lambda > 0,$$

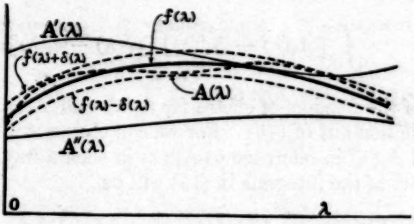

FIGURE 2.

and let δ be any quantity > 0. We say then that the functions $A(\lambda)$ are densely distributed between $A'(\lambda)$ and $A''(\lambda)$ provided that no matter what $f(\lambda)$ and δ are taken, there is an $A(\lambda)$ such that

$$|f(\lambda) - A(\lambda)| \leqq \delta, \quad 0 < \lambda.$$

We shall assume that $A_1(\lambda)$ and $A_2(\lambda)$ are independently densely distributed between two functions $A_1'(\lambda)$ and $A_1''(\lambda)$, and two functions $A_2'(\lambda)$ and $A_2''(\lambda)$ respectively, where

$$A_1''(\lambda) > A_1'(\lambda), \quad 0 < \lambda,$$

and

$$A_2''(\lambda) > A_2'(\lambda), \quad 0 < \lambda.$$

Suppose now that $e_1'(\lambda) \neq e_1(\lambda)$ at some value

$$\lambda = \lambda_0, \quad 0 < \lambda_0.$$

It will then be unequal to $e_1(\lambda)$ throughout a small neighborhood $\lambda_1 \leqq \lambda \leqq \lambda_2$, — let us say that $e_1'(\lambda) - e_1(\lambda) > \epsilon > 0$ throughout the interval.

Now if we subtract (12) from (13) we have

$$\int_0^\infty A_1(\lambda)\,[e_1'(\lambda) - e_1(\lambda)]\,d\lambda + \int_0^\infty A_2(\lambda)\,[e_2'(\lambda) - e_2(\lambda)]\,d\lambda = 0. \quad (14)$$

In particular we have

$$\int_0^\infty A_1'(\lambda)\,[e_1'(\lambda) - e_1(\lambda)]\,d\lambda + \int_0^\infty A_2'(\lambda)\,[e_2'(\lambda) - e_2(\lambda)]\,d\lambda = 0,$$

whence

$$\int_0^\infty [A_1(\lambda) - A_1'(\lambda)]\,[e_1'(\lambda) - e_1(\lambda)]\,d\lambda + \int_0^\infty [A_2(\lambda) - A_2'(\lambda)]\,[e_2'(\lambda) - e_2(\lambda)]\,d\lambda = 0. \quad (15)$$

On account of the freedom of choice for $A_1(\lambda)$ and $A_2(\lambda)$ we can now get a contradiction out of (15). For we can choose $A^1(\lambda)$ in reference to $A_1'(\lambda)$ and $A_2(\lambda)$ in reference to $A_2'(\lambda)$ in such a way that the only significant part of the integrals in (15) will be

$$\int_{\lambda_1}^{\lambda_2} [A_1(\lambda) - A_1'(\lambda)]\,[e_1'(\lambda) - e_1(\lambda)]\,d\lambda,$$

which can be made unequal to zero. But this contradicts (15). Hence $e_1'(\lambda_0) = e_1(\lambda_0)$ and $e_1'(\lambda) \equiv e_1(\lambda)$.

And not only for every body S but also for every position of Σ_0 in the cavity is $e_1'(\lambda) \equiv e_1(\lambda)$. For different positions of Σ_0 can be regarded as the same position of Σ_0 with different S. Hence in particular $e_1(\lambda) = e_2(\lambda)$. We have then the theorem that the character of the radiation impinging on either face of any element of surface σ anywhere in the cavity S is a function merely of the temperature of the cavity and the nature of the medium in which the element of surface is immersed.

If we denote the function $e_1(\lambda) = e_2(\lambda)$ by $e(\lambda)$, we may call $e(\lambda)$ perfectly black radiation. It is approximately the radiation emitted through a hole of unit area in the bounding surface of a large cavity whose interior walls are kept at the uniform temperature T.

We can now easily prove Kirchhoff's Law. Suppose that in the cavity S we have any body K, enclosed by a surface S, just outside the

surface of K. A surface S_1' is assumed outside S_1; between K and S_1' there is an arbitrary medium. K itself may be solid, liquid or gaseous, though if K is liquid or gaseous the medium in which it is enclosed must be solid. We have then, at the temperature T,

$$\int\int_{(S_1)} E(\lambda)\, dS_1 + \int\int_{(S_1)} [1 - A(\lambda)]\, e(\lambda)\, dS_1 = \int\int_{(S_1)} e(\lambda)\, dS_1 \tag{17}$$

since the amount of radiation of wave length λ reaching any element of surface dS, *from either side* is $e(\lambda)$.

Hence

$$\int\int_{(S_1)} E(\lambda)\, dS_1 = \int\int_{(S_1)} A(\lambda)\, e(\lambda)\, dS_1, \tag{18}$$

which is an expression of Kirchhoff's Law. The expression looks more natural if we denote by $\overline{A}(\lambda)$

$$\overline{A}(\lambda) = \frac{\int\int_{(S_1)} A(\lambda)\, e(\lambda)\, dS_1}{\int\int_{(S_1)} e(\lambda)\, dS_1};$$

we then have

$$\int\int_{(S_1)} E(\lambda)\, dS_1 = \overline{A}(\lambda) \int\int_{(S_1)} e(\lambda)\, dS_1. \tag{19}$$

If the $E(\lambda)$ is a function of the element of surface only, we can by taking a spherical K of the material under investigation deduce from symmetry that

$$E(\lambda) = A(\lambda)\, e(\lambda).$$

Discussion of the Assumptions.

On page 99 certain assumptions are made in regard to the functions $\delta_{\sigma_1}(\lambda)$ and $\delta_{\sigma_2}(\lambda)$,— namely, that as the body Σ_0 decreases in size, $\delta_{\sigma_1}(\lambda)$ and $\delta_{\sigma_2}(\lambda)$ approach zero as a limit in such a way that

$$\Delta_{\sigma_1} = \int_0^\infty | \delta_{\sigma_1}(\lambda) |\, d\lambda$$

and

$$\Delta_{\sigma_2} = \int_0^\infty | \delta_{\sigma_2}(\lambda) |\, d\lambda$$

both approach zero. This amounts in effect to assuming that

$\sigma(\Delta_{\sigma_1} + \Delta_{\sigma_2})$, the difference in the radiation reaching the surface Σ_0 when there is and when there is not a different material in Σ_0 from the medium between Σ_0 and Σ_1, is an infinitesimal of the second order. This supposition seems more reasonable than it really is.

For let us suppose, if it is possible, that the body S is composed of a material which emits and absorbs only a partial spectrum, i.e. there are wave lengths for which S emits and absorbs no energy. With no body Σ_0 and ether for the medium throughout, the radiation $e(\lambda)$ reaching any element of surface within the cavity will not contain energy of these wave lengths which the body S does not emit. But if we insert a body Σ_0, however small, which has a complete spectrum, the energy of the forbidden wave lengths will build up until it reaches such intensity that the amount absorbed by the small body Σ_0 will be equal to the amount emitted by it. Since both of these quantities will therefore be infinitesimals of the first order, $\delta_1(\lambda)$ and $\delta_2(\lambda)$ will not approach zero at all as Σ_0 decreases in size.

We cannot therefore regard the invariance of the function $e(\lambda)$ as itself a statement of the non-existence of bodies of partial spectra.[5] For that invariance depends upon the assumption that Δ_{σ_1} and Δ_{σ_2} approach zero as Σ_0 becomes smaller and smaller, and hence gives no contradiction when S is a body of partial spectrum.

However, bodies of partial spectra, if they exist, must satisfy Kirchhoff's Law. For the analysis of pages 101 and 102 applies. And a body that has a partial emission spectrum must have an absorption spectrum extending over precisely the same region of wave lengths; and vice versa.

The second assumption of importance is the supposition that there can be constructed a dense distribution of absorption coefficients between some two distinct functions of λ. This assumption does not by any means demand the existence of an arbitrary absorption coefficient. Indeed the requirements of the proof can be met by a denumerable system[6]. And yet we cannot be certain of the possibility of physically constructing even this denumerable set.

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[5] See, however, in this connection W. Wien, Annalen d. Physik, **52**, 163, 1894.

[6] That is, a system of the same order of infinity as the natural numbers, or the rational fractions.

If $A'(\lambda)$ and $A''\lambda$) (see p. 8) have the same limit at ∞, a denumerable set sufficient for the demands of the proof can be set up by requiring that $f(\lambda)$ be continuous with continuously turning tangent (except at a finite number of points), and by replacing, in the definition of density, the two curves $f(\lambda) \pm \delta(\lambda)$ by two curves distant δ from the curve $f(\lambda)$.

Although the present proof depends, indeed, on this assumption of the physical existence of ideal elements, the proof is not completely invalidated by the lack of such a system. There is in this instance the considerable advantage that the existence of even a finite physical system approximately fulfilling the conditions of the postulated ideal system carries with it the approximate fulfilment of the thesis. Kirchhoff's Law is approximately satisfied in any case.

It is worth while noting that, although establishing a particular property of any particular substance, namely that its emission and absorption coefficient must stand in a certain fixed relation, the proof, on account of its nature, holds only in so far as the particular substance is a member of a physical system that contains as a subset the dense system postulated.[7] The properties of the individual are determined by the environment.

Finally there is a third assumption that needs some attention. For on page 103, in deducing equation (17), which holds for any particular value of λ, it is assumed that the wave length of energy is unchanged by reflection. And Kirchhoff's Law will therefore hold for any bodies whose surfaces are such that they do not change wave length by reflection.

In certain cases this assumption about the nature of the body itself is equivalent to a condition on the environment. For if the body under consideration be a member of a dense system of absorption coefficients, the above assumption may be replaced by postulating that a single member of that system be known to obey Kirchhoff's Law. And from this postulate the other, that wave length be unchanged by reflection, may be deduced. The two, though they do not look alike, are in a sense mathematically equivalent.

Conclusion.

The fruitfulness of Kirchhoff's Law depends upon the degree to which the absorption coefficient is invariant in regard to different conditions of the body or its surroundings, i.e., for instance in regard to (1) different temperatures of the absorbing body, and (2) different in-

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[7] Some proofs err in assuming the existence of bodies of partial spectra or in attempting to construct them; e. g.: Kirchhoff (1859) and Drude (1900).

In regard to other proofs it may be noted that those of B. Stewart and Prevostaye are not logically complete, and that Kirchhoff's second proof, besides being involved, is not strictly thermodynamic and assumes the existence of bodies with questionable properties.

For detailed references see Kayser's Spectroscopie II, pages 7–31.

tensities of radiation reaching the surface from outside [corresponding to different temperatures of the body S]. For in general the absorption coefficient has to be measured under one set of conditions when it is desired to apply the results to another set.

Hence it may seem that Kirchhoff's Law holds very well for one set of bodies and very poorly for another set, if the absorption coefficient is regarded as a constant. The preceding analysis shows, however, that carefully stated, the law holds as well for one substance as another, as well for gases and liquids as for solids.

In closing I should like to acknowledge my indebtedness to Professor G. W. Pierce of Harvard University for helpful criticism.

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